

Serial No.: 10/054,742

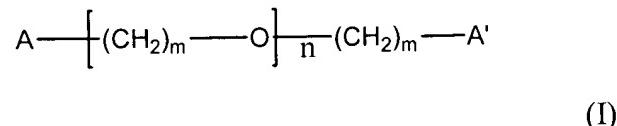
Filed: January 22, 2002

Title: SHAPE MEMORY POLYURETHANE OR POLYURETHANE-UREA POLYMERS

CLEAN VERSION OF PENDING CLAIMS

77. A shape memory polyurethane or polyurethane-urea polymer including a reaction product of (a), (b) and (c) as set out under (A) below, a reaction product of (b) and (c) as set out under (B) below or a reaction product of (b) and (d) as set out under (C) below:

(A) (a) silicon based macrodiol, silicon-based macrodiamine and/or polyether of the formula (I):



wherein

A and A' are endcapping groups;

m is an integer of 6 or more; and

n is an integer of 1 or greater;

(b) a diisocyanate; and

(c) a chain extender,

(B) (d) a diisocyanate;

(c) a chain extender; and

no soft segment; or

(C) (b) a diisocyanate; and

(d) a silicon-containing chain extender,

said polymer having a glass transition temperature which enables the polymer to be transformed from its original shape into a first shape at a temperature higher than the glass transition temperature and maintained in said first shape when the polymer is cooled to a temperature lower than the glass transition temperature, said polymer then being capable of resuming its original shape on heating to a temperature higher than the glass transition temperature.

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78. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein component (a) is a combination of at least two macrodiols, at least two macrodiamines or at least one macrodiol and at least one macrodiamine.

79. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein component (a) has greater than about 50% silicon-based macrodiol.

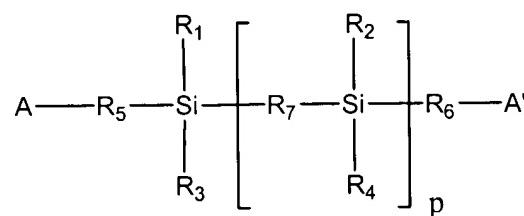
80. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein component (a) has greater than about 70% silicon based macrodiol.

81. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the molecular weight range of component (a) is about 300 to about 2000.

82. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the molecular weight range of component (a) is about 300 to about 700.

83. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the silicon-based macrodiol or macrodiamine is a polysilane, polysiloxane, amino-terminated polysiloxane or a silicon-based polycarbonate.

84. A shape memory polyurethane or polyurethane-urea polymer according to claim 83, wherein the polysiloxane or amino-terminated polysiloxane is represented by the formula (II):



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(II)

wherein

A and A' are as defined in claim 77:

R₁, R₂, R₃, R₄, R₅ and R₆ are the same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

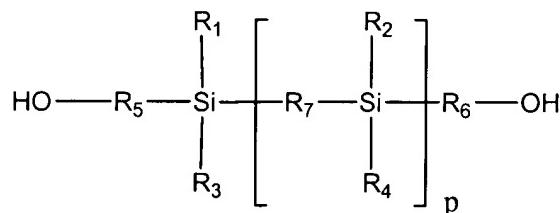
R₇ is a divalent linking group or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical; and

p is an integer of 1 or greater.

85. A shape memory polyurethane or polyurethane-urea polymer according to claim 84, wherein the divalent linking group for R₇ is O, S or NR wherein R is hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical.

86. A shape memory polyurethane or polyurethane-urea polymer according to claim 84, wherein the polysiloxane is a polysiloxane macrodiol which is a polymer of the formula (II) wherein R and R' are hydroxy.

87. A shape memory polyurethane or polyurethane-urea polymer according to claim 86, wherein the polysiloxane macrodiol is represented by the formula (III):



(III)

wherein

R₁ to R₆ are as defined in claim 84.

88. A shape memory polyurethane or polyurethane-urea polymer according to claim 87, wherein the macrodiol is PDMS which is a compound of formula (III) wherein R₁ to R₄ are methyl and R₅ and R₆ are as defined in claim 87.

89. A shape memory polyurethane or polyurethane-urea polymer according to claim 87, wherein R₅ and R₆ are the same or different and selected from propylene, butylenes, pentylene, hexylene, ethoxypropyl (-CH₂CH₂OCH₂CH₂CH₂-), propoxypropyl and butoxypropyl.

90. A shape memory polyurethane or polyurethane-urea polymer according to claim 86, wherein the molecular weight range of the polysiloxane macrodiol is about 200 to about 6000.

91. A shape memory polyurethane or polyurethane-urea polymer according to claim 86, wherein the molecular weight range of the polysiloxane macrodiol is about 500 to about 2000.

92. A shape memory polyurethane or polyurethane-urea polymer according to claim 84, wherein the amino-terminated polysiloxane is a polysiloxane macrodiamine which is a polymer of the formula (II) wherein A is NH₂.

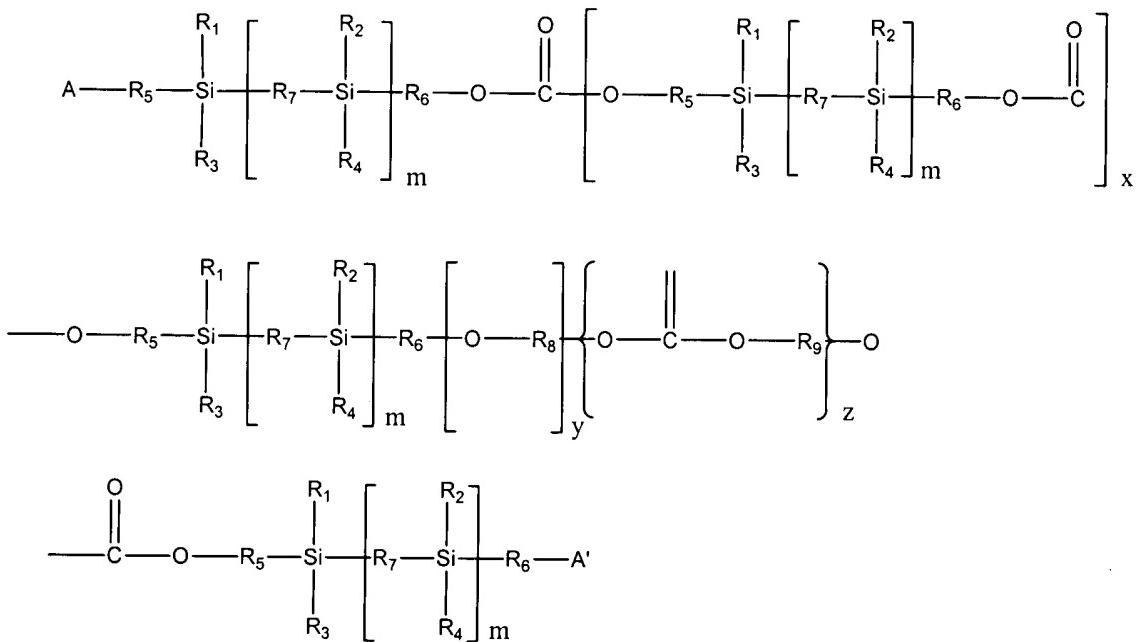
93. A shape memory polyurethane or polyurethane-urea polymer according to claim 92, wherein the polysiloxane macrodiamine is amino-terminated PDMS.

94. A shape memory polyurethane or polyurethane-urea polymer according to claim 83; wherein the silicon-based polycarbonate has the formula (IV):

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(IV)

wherein:

R₁, R₂, R₃, R₄, R₅, R₆ and R₇ are as defined in formula (II) in claim 84;R₈ and R₉ are same or different and selected from hydrogen or an optionally substituted straight chain, branched or cyclic, saturated or unsaturated hydrocarbon radical;

A and A' are as defined in formula (I) in claim 77;

m, y and z are integers of 0 or more; and

x is an integer of 0 or more.

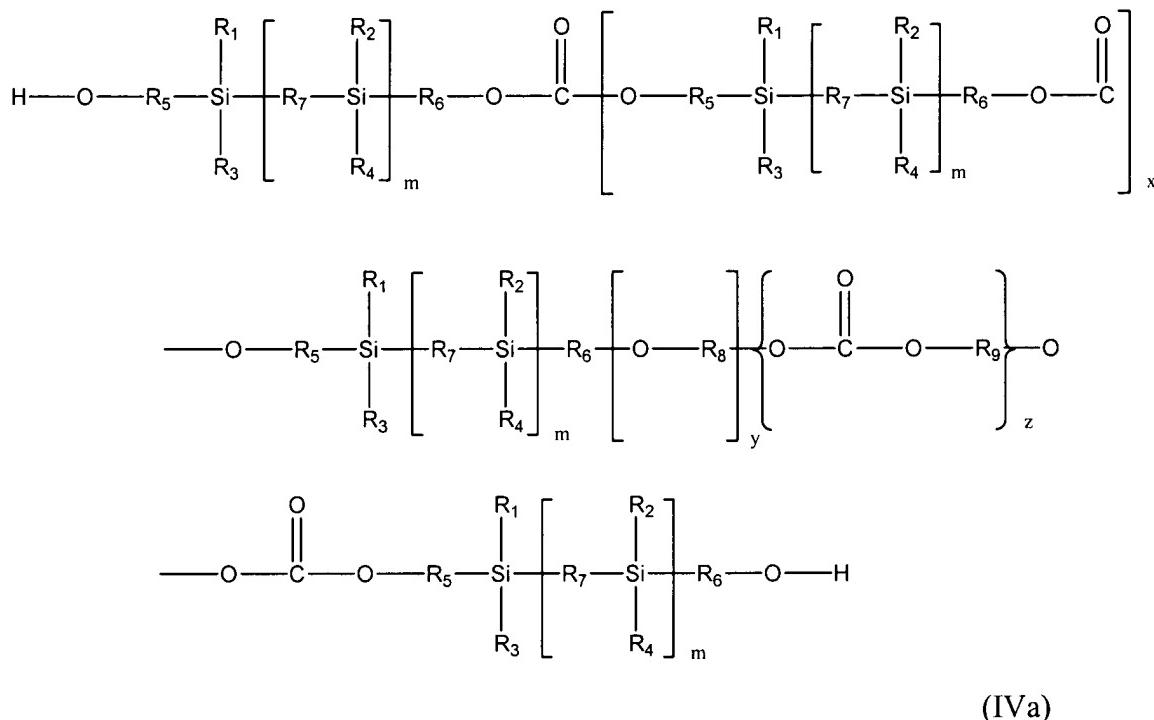
95. A shape memory polyurethane or polyurethane-urea polymer according to claim 94, wherein z is an integer of 0 to about 50, x is an integer of 1 to about 50, m is an integer of 0 to about 20 and y is an integer of 0 to about 10.

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96. A shape memory polyurethane or polyurethane-urea polymer according to claim 94, wherein the silicon-based polycarbonate is a compound of the formula (IV) wherein the endcapping group is a hydroxy which is a polycarbonate macrodiol of the formula (IVa):



wherein

R_1 to R_9 , m , y , x and z are as defined in formula (IV) in claim 18.

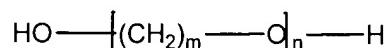
97. A shape memory polyurethane or polyurethane-urea polymer according to claim 96, wherein the polycarbonate macrodiol is a compound of the formula (IVa) wherein R_1 , R_2 , R_3 and R_4 are methyl, R_8 is ethyl, R_9 is hexyl, R_5 and R_6 are propyl or butyl and R_7 is O or $-\text{CH}_2\text{---CH}_2-$.

98. A shape memory polyurethane or polyurethane-urea polymer according to claim 97 wherein R_5 and R_6 are propyl when R_7 is O and R_5 and R_6 are butyl when R_7 is $-\text{CH}_2\text{---CH}_2-$.

99. A shape memory polyurethane or polyurethane-urea polymer according to claim 96, wherein the molecular weight range of the polycarbonate macrodiol is about 400 to about 5000.

100. A shape memory polyurethane or polyurethane-urea polymer according to claim 96, wherein the molecular weight range of the polycarbonate macrodiol is about 400 to about 2000.

101. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the polyether is a polyether macrodiol represented by the formula (V):



(V)

wherein

m is as defined in formula (I) in claim 77; and

n is as defined in formula (I) in claim 77.

102. A shape memory polyurethane or polyurethane-urea polymer according to claim 101, wherein the polyether macrodiol is poly(tetramethylene oxide) (PTMO), poly(hexamethylene oxide) (PHMO), poly(heptamethylene oxide), poly(octamethylene oxide) (POMO) or poly(decamethylene oxide) (PDMO).

103. A shape memory polyurethane or polyurethane-urea polymer according to claim 101, wherein the molecular weight range of the polyether macrodiol is about 300 to about 2000.

104. A shape memory polyurethane or polyurethane-urea polymer according to claim 101, wherein the molecular weight range of the polyether macrodiol is about 300 to 700.

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105. A shape memory polyurethane or polyurethane-urea polymer according to claim 88, wherein component (a) is a combination of PDMS or amino-terminated PDMS with another polymer falling within the scope of component (a).

106. A shape memory polyurethane or polyurethane-urea polymer according to claim 105, wherein said another polymer is a polyether of the formula (I) or a silicon based polycarbonate.

107. A shape memory polyurethane or polyurethane-urea polymer according to claim 106, wherein the polyether of the formula (I) is PHMO.

108. A shape memory polyurethane or polyurethane-urea polymer according to claim 106, wherein the silicon-based polycarbonate is a siloxy carbonate.

109. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the diisocyanate is an aliphatic or aromatic diisocyanate.

110. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the diisocyanate is 4,4'-diphenylmethane diisocyanate (MDI), methylene biscyclohexyl diisocyanate (H₁₂MDI), p-phenylene diisocyanate (p-PDI), trans-cyclohexane-1,4-diisocyanate (CHDI), 1,6-diisocyanatohexane (DICH), 1,5-diisocyanatonaphthalene (NDI), para-tetramethylxylenediisocyanate (p-TMXDI), meta-tetramethylxylene diisocyanate (m-TMXDI), 2,4-toluene diisocyanate (2,4-TDI) isomers or mixtures thereof or isophorone diisocyanate (IPDI).

111. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the diisocyanate is MDI.

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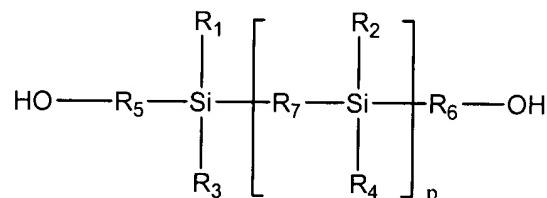
112. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the chain extender is a diol or diamine chain extender.

113. A shape memory polyurethane or polyurethane-urea polymer according to claim 112, wherein the diol chain extender is 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, 1,12-dodecanediol, 1,4-cyclohexanediol, 1,4-cyclohexanedimethanol, p-xleneglycol, 1,3-bis(4-hydroxybutyl)tetramethyldisiloxane, 1,3-bis(6-hydroxyethoxypropyl)tetramethyldisiloxane or 1,4-bis(2-hydroxyethoxy)-benzene.

114. A shape memory polyurethane or polyurethane-urea polymer according to claim 112, wherein the diamine chain extender is 1,2-ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, 1,3-bis(3-aminopropyl)tetramethyldisiloxane, 1,3-bis(4-aminobutyl)tetramethyldisiloxane or 1,6-hexanediamine.

115. A shape memory polyurethane or polyurethane-urea polymer according to claim 112, wherein the chain extender is a silicon-containing chain extender.

116. A shape memory polyurethane or polyurethane-urea polymer according to claim 115, wherein the silicon-containing chain extender includes a silicon-containing diol of the formula (VI):



(VI)

wherein

$\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{R}_6$ and R_7 are as defined in formula (II) in claim 84; and

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q is 0 or greater.

117. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein component (a) polymer forms the soft segment of the polyurethane or polyurethane-urea polymer.

118. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein components (b) and (c) of the polymer form the hard segment of the polyurethane or polyurethane-urea polymer.

119. A shape memory polyurethane or polyurethane-urea polymer according to claim 118, wherein the amount of hard segment in the polymer is about 30 to 100wt%.

120. A shape memory polyurethane or polyurethane-urea polymer according to claim 118, wherein the amount of hard segment in the polymer is about 50 to 80 wt%.

121. A shape memory polyurethane or polyurethane-urea polymer according to claim 118, wherein the amount of hard segment in the polymer is about 60 to about 70 wt%.

122. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the shore hardness of the polymer below the glass transition temperature is in the range of about 82D to about 50D, while the hardness above the glass transition temperature is in the range of about 20D to about 30D.

123. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the glass transition temperature is in the range of about 20°C to about 100°C.

124. A shape memory polyurethane or polyurethane-urea polymer according to claim 77, wherein the glass transition temperature is in the range of about 20°C to about 60°C.

125. A shape memory composition which includes a blend of two or more of the shape memory polyurethane or polyurethane-urea polymers defined in claim 77 or at least one shape memory polyurethane or polyurethane-urea polymer defined in claim 77 in combination with another material.

126. A shape memory composition according to claim 125, wherein the other material is a polymeric or a non-polymeric material.

127. A shape memory composition according to claim 126, wherein the polymeric material is a conventional polyurethane, shape memory polyurethane, polyolefin, polyamide or a liquid crystalline polymer.

128. A shape memory composition according to claim 125, wherein each of the polymers forming the shape memory composition have different glass transition temperatures and/or different amount of hard segment component.

129. A shape memory composition according to claim 128, which includes a first polymer with a low glass transition temperature of below about ambient temperature and a second polymer with a glass transition temperature above the ambient temperature.

130. A shape memory composition according to claim 128, wherein the two polymers can be blended in proportions such that the final blend will have a glass transition temperature in the range of about 20°C to about 60°C.

131. A shape memory composition according to claim 128, which includes a first polymer having a high percentage of hard segment component of above about 70 wt% and a second polymer having a lower percentage of hard segment of about 30wt% to about 60wt%.

132. A shape memory composition according to claim 131, wherein the composition includes a combination of an elastomeric and a non-elastomeric polyurethane or polyurethane-urea polymer.

133. A process for preparing a shape memory polymer as defined in claim 77 which includes the steps of:

- (i) mixing component (a) and the chain extender (c); and
- (ii) reacting the mixture with the diisocyanate (b).

134. A process according to claim 133, wherein step (i) is performed at a temperature in the range of about 45°C to about 100°C.

135. A process according to claim 133, wherein step (i) occurs in the presence of a catalyst.

136. A process for preparing a shape memory polymer as defined in claim 77 which includes the steps of:

- (i) reacting component (a) with a diisocyanate (b) to form a prepolymer; and
- (ii) reacting the prepolymer with the chain extender (c).

137. A material having improved mechanical properties, clarity, processability, biostability and/or degradation resistance which includes the shape memory polymer as defined in claim 77 and/or the composition as defined in claim 125.

138. A material according to claim 137, wherein the improved mechanical properties are tensile strength, tear strength, flex fatigue resistance, abrasion resistance, Durometer hardness, flexural modulus and/or related measures of flexibility or elasticity.

139. A material according to claim 137, wherein the improved resistance to degradation is resistance to free radical, oxidative, enzymatic and/or hydrolytic processes and/or to degradation when implanted as a biomaterial.

140. A material according to claim 137, wherein the improved processability is ease of processing by casting and/or thermal means.

141. A material according to claim 137, which is a biostable material.

142. A material according to claim 137, which is a degradation resistant material.

143. A material according to claim 137, which is an *in vivo* degradation resistant or biostable material.

144. A material according to claim 137, which is a biomaterial.

145. Use of the shape memory polymer as defined in claim 77 and/or composition as defined in claim 125 as a material having improved mechanical properties, clarity, processability, biostability and/or degradation resistance.

146. The shape memory polymer as defined in claim 77 and/or composition as defined in claim 125 when used as a material having improved mechanical properties, clarity, processability, biostability and for degradation resistance.

147. A device or article which is composed wholly or partly of the shape memory polymer as defined in claim 77 and/or composition as defined in claim 125.

148. A device or article according to claim 147, which is a medical device, article or implant.

149. A device or article according to claim 148, which is a stylet; bone suture anchor; vascular, esophageal or biliary stent; cochlear implant; reconstructive facial surgery; controlled drug release device; component in key-hole surgery; biosensor; membrane for cell encapsulation; medical guidewire; medical guidepin; cannularization; pacemaker, defibrillator or neurostimulator and their respective electrode leads; ventricular assist device; orthopedic joint or parts thereof; intraocular lens; urological device; stent/graft device; device joining/extending/repair sleeves; heart valve; vein graft; vascular access port; vascular shunt; blood purification device; cast for a broken limb; vein valve, angioplasty, electrophysiology or cardiac output catheter; or tools for insertion of medical devices, infusion and flow control devices.

150. A device or article according to claim 147, which is a toy or component thereof, shape memory film, pipe coupling, electrical connector, zero-insertion force connector, robotic, aerospace actuator, dynamic display, flow control device, sporting goods and components thereof, body-conforming device, temperature control device, safety release device or heat shrink insulation.

151. Use of the shape memory polymer as defined in claim 77 and/or composition as defined in claim 125 in the manufacture of a device or article.

152. A shape memory polymer as defined in claim 77 and/or a composition as defined in claim 124 when used in manufacture of a device or article.